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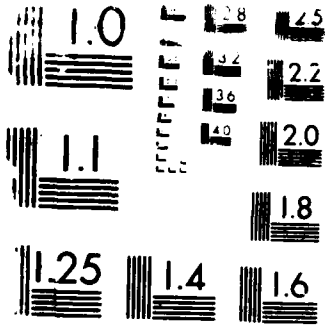
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Optically Nonlinear Polymeric Materials

R. C. Hall, Final Technichal Report

N00014-83-D-0689

## Introduction.

The nonlinear optical polymer project has been fairly successfull. Several new materials have been synthesized and characterized, some of which may be of considerable use to the Navy. Two papers have been submitted and accepted, and an invention disclosure has been made (a patent applications should follow within the next year). Research proposals have been submitted to DARPA, NSF, and the Night Vision Laboratory (Army) to allow research in optical polymers at the Naval Weapons Center to be expanded and include more scientists.

Second order nonlinear optical polymers require processing into films having highly ordered noncentrosymmetric arrangements such as can be found in a crystal lattice. I have chosen the Langmuir-Blodgett (L/B) technique for fabrication of noncentrosymmetric polymer films.

The L/B method is well suited for making highly ordered thin films of organic materials. This method requires use of amphiphilic molecules having a water soluble head group and a hydrophobic tail group such as a long chain fatty acid. The amphiphiles are spread on the water surface of a L/B trough (Figure 1). The hydrophilic head group sits on the water surface, while the hydrophobic alkyl tails orient themselves away from the water. By moving a barrier across the water surface and compressing the molecules, an organized monolayer is formed. A substrate is dipped through the monolayer, transferring it to the substrate. Subsequent dipping of this coated substrate through new monolayers builds a multilayered film (Figure 2). I have prepared surfactant polymers having a hydrophilic backbone and hydrophobic substituents to form L/B polymers. By covalently incorporating nonlinear optical chromophores into the hydrophobic portions of the polymer, second order nonlinear optical effects may be obtained.

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## Experimental

Several of my early experiments showed that monomers containing groups with large molecular hyperpolarizabilities such as 4-nitroanilines, 4-amino-4'-nitrostilbenes, and stilbazolium hemicyanines are often unreactive towards radical or ionic polymerization or give poor conversion to polymer. The chemical attachment of polarizable dye groups to preformed polymers, however, avoids these problems.

A new class of polyethers containing optically nonlinear hemicyanine dyes has been prepared that is specifically designed for processing into L/B films. The



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synthesis of these polymers is based on chemical modification of commercially available poly(epichlorohydrin) (PECH) resins. Two types of dye-substituted polyether have been synthesized; in one case the electron donating end of the chromophore is adjacent to the polymer backbone, and in the second case the electron withdrawing end is adjacent to the backbone.

Polyethers with the backbone adjacent to the electron donating end of the dye were prepared by alkylation of phenolic aldehydes with the chloromethyl groups along the PECH backbone to make alkoxybenzaldehyde susbstituted polymers, as shown in Scheme I. This was carried out by refluxing a solution of PECH with excess 4-hydroxy-benzaldehyde, anhydrous potassium carbonate, and a phase-transfer catalyst in acetonitrile for 4 days. After reprecipitation in methanol, proton NMR analysis showed up to 50% substitution of the aldehyde along the backbone. Condensation of the aldehyde-substituted polymers with long chain ($C_{12}$, $C_{16}$, $C_{18}$) alkyl-picolinium bromides by refluxing in acetonitrile for 16 hours with a trace of piperidine yielded hemicyanine-substituted PECHs. Proton NMR showed all of the aldehyde sites had reacted to give up to 50% dye substitution.

Placing the electron withdrawing end of the hemicianine adjacent the backbone was achieved by quaternizing the nitrogen on 4-picoline with the PECH chloromethyl groups, as shown in Scheme II. This was acheived by heating PECH with an excess of 4-picoline in acetonitrile for 10 days. In this case proton NMR showed about one third of the backbone sites to be occupied by picolinium chloride groups. Condensation of this polymer with a long chain ($C_{18}$)-alkoxybenzaldehyde resulted in a hemicyanine-substituted polymer.

These polymers are chloroform soluble, deep red colored glasses. The chromophores absorb visible light wth a lambda maximum of 390 nm and an absorption edge near 500 nm ($10^{-4}$ M in chloroform), making them transparent to doubled $Nd^{+3}$-YAG laser light at 532 nm.

The picolinium chloride-substituted polyether of Scheme II has also been reacted with trans-4-N,N-dimethylamino-cinnamaldehyde, giving the polymer shown in Figure 3. This chromophore should have greater optical nonlinearity because of its better electron donating dimethylamino group and its longer conjugation length. In this case the extended hemicyanine chromophore acts as the hydrophobic portion of the polymer.

Trans retinal also reacts with the picolinium chloride-substituted polymer to place a rhodopsin-like chromophore on the polymer backbone (Figure 4).

I have prepared the maleimide-allyl hemicyanine copolymer shown in Scheme III by 1:1 alternating copolymerization of maleimide with allyl picolinium bromide, followed by condensation with a $C_{18}$-alkoxybenzaldehyde. Thermal and Molecular weight characterization of this

polymer has not yet ben carried out. This type of polymer does not have any unsubstituted portions along the polymer backbone as do the PECH-hemicyanines.

The thermal behavior of the PECH-hemicyanines shown in Schemes I and II was investigated by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and by visual observation while heating and cooling under a polarizing microscope. All polymers investigated showed fairly complex decomposition patterns by DSC, typically showing the onset of an exotherm (decomposition) at about 150°, followed by an endotherm near 200° indicating some softening of the polymer glasses. At about 250° all polymer samples showed the onset of major thermal decomposition which was verified by visual observation as well as TGA. No evidence of liquid crystalline behavior for PECH-hemicyanines was found, though the possibility was recognized that the unsubstituted portions of PECH backbone may act as spacers for the rigid mesogenic chromophores.

The Langmuir-Blodgett film formation was carried out by Brian Anderson of the U. C. Davis Department of Chemical Engineering. All L/B depositions were carried out at a surface pressure of 30-35 mN/m. Deposition stroke speed was 0.6 cm/min. Monolayers of hemicyanine-substituted PECH of Scheme I (polymer A) were spread from chloroform onto pure glass-distilled water. Polymer A was deposited onto two back-to-back clean glass slides on the upstroke. The subphase surface was cleaned and either behenic acid ($C_{22}$) or the PECH hemicyanine of Scheme II (polymer B) was deposited on the downstroke, resulting in alternating layers of polymer A with Polymer B or behenic acid. This alternating method, shown in Figures 5 and 6, resulted in formation of noncentrosymmetric multilayers.

## Results and Discussion

Figure 7 shows the surface pressure vs. surface area (pi-A) curve for both types of hemicyanine-substituted PECH at 22° C. During monolayer compression of polymer A the pi-A curve exhibits a plateau between 20 and 30 dynes/cm, then shows a steep slope until the monolayer collapses near 45 dynes/cm. This plateau may be due to the positively charged group at the top of the hemicyanine dye. At pressures below 20 dynes/cm the dyes could lie down on the subphase surface to solvate the charged species, resulting in a "log-jam" of horizontal chromophores in the compressed monolayer. Above 20 dynes/cm the dyes may stand up more vertically relative to the subphase. In polymer B the charged group is next to the backbone and the pi-A curve does not show a plateau.

Second harmonic generation (SHG) in PECH-hemicyanines was measured at U. C. Davis by passing $Nd^{+3}$-YAG laser light (1064 nm) through mono- and multilayer films on a glass slide and detecting the second harmonic (532 nm) light with a photomultipier. The increase in relative second harmonic

intensity with additional layers of polymer A interleaved with behenic acid is shown in Figure 8. The enhancement of SHG intensity is roughly quadratic (within error bars) for the first three layers of polymer. Figure 9 shows second harmonic enhancement vs. number of bilayers of interleaved polymers A and B, indicating quadratic SHG icrease for eight polymer layers (four bilayers).

The PECH substituted with the extended chromophore (Figure 3) has been investigated optically as a monolayer on the water surface of a L/B trough. SHG from a single layer of this polymer is approximately 80 times greater than from a monolayer of polymers A or B.

Film fabrication and optical measurements have not yet been carried out for the PECH containing the rhodopsin-like chromophore (Figure 4) and the maleimide-allyl hemicyanine polymer of Scheme III.

Langmuir-Blodgett Second Harmonic Generation

## Conclusion

A new class of optically nonlinear hemicyanine-substituted PECH polymers has been synthesized and processed into noncentrosymmetric (L/B) films that exhibit strong SHG. Quadratic enhancement of (SHG) has been achieved up to eight monomolecular layers, more than in any other material yet reported in the literature.

Increasing the optical nonlinearity of the attached chromophore by extending the pi-electron system and changing the electron donating group have increased the SHG efficiency of a monolayer by nearly a factor of 100.

If further improvements in chromophore optical nonlinearity and quadratic enhancement can be achieved in a greater number of layers, these films may someday be an alternative to currently used inorganic crystalline laser frequency doublers.

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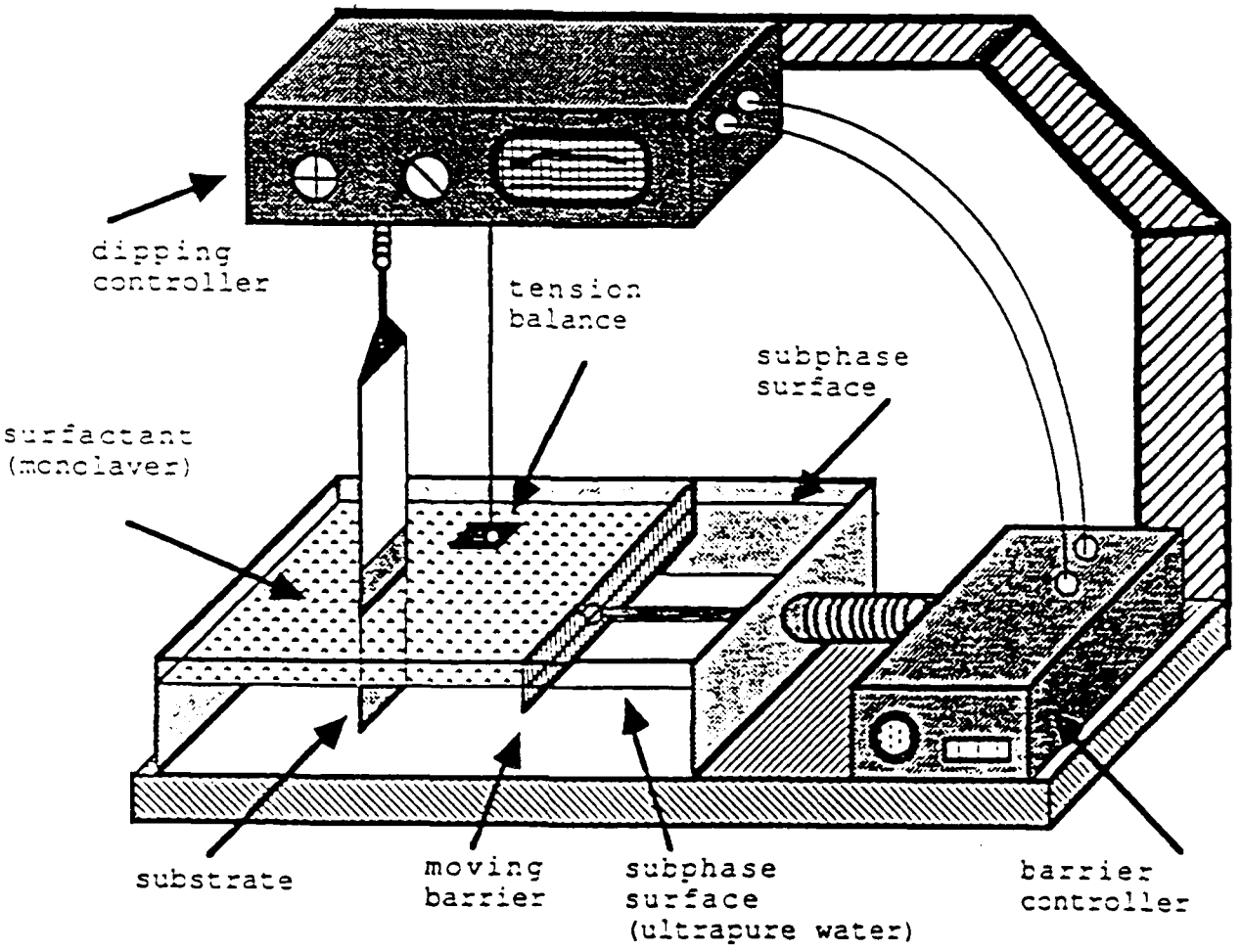



Figure 1. Simplified diagram of a Langmuir-Blodgett trough for fabrication of thin polymer films.

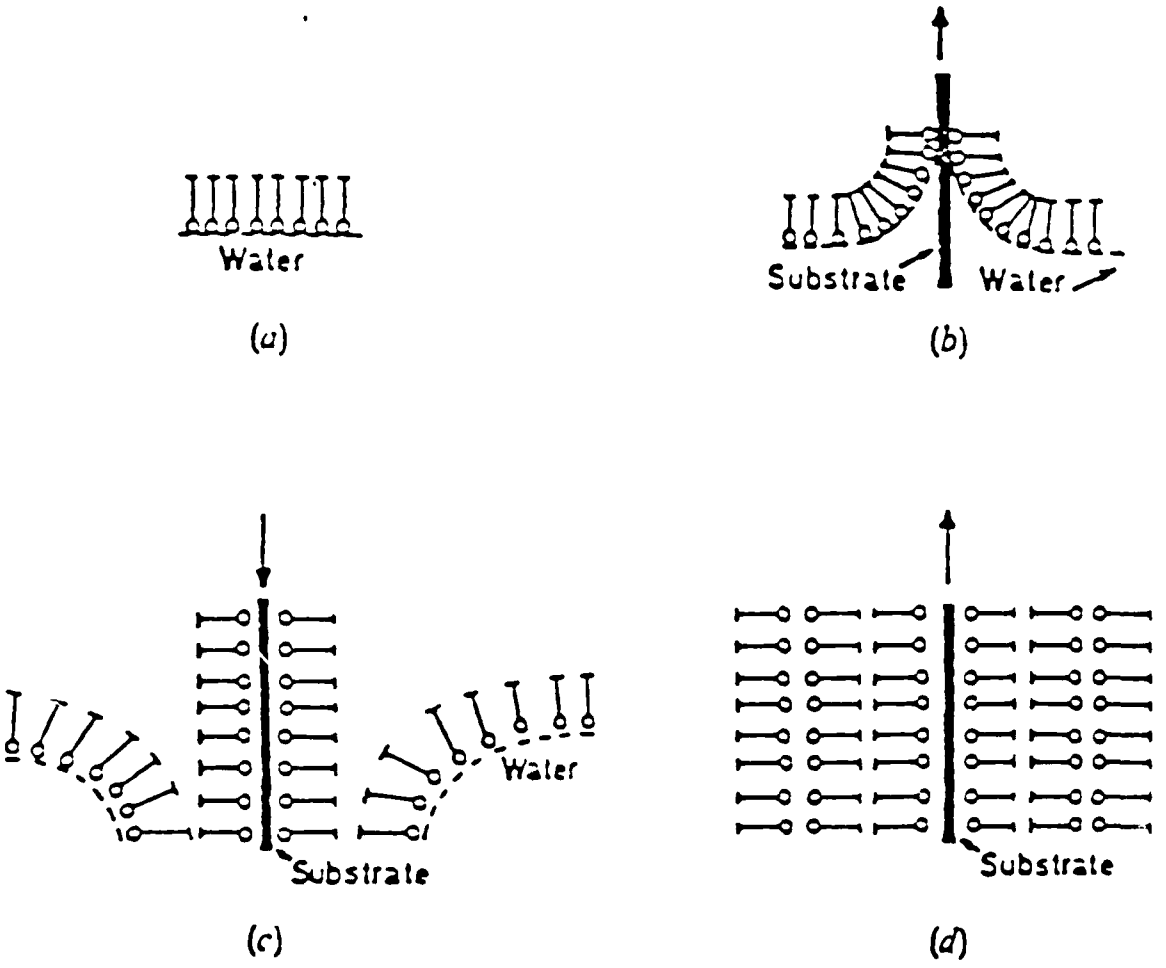
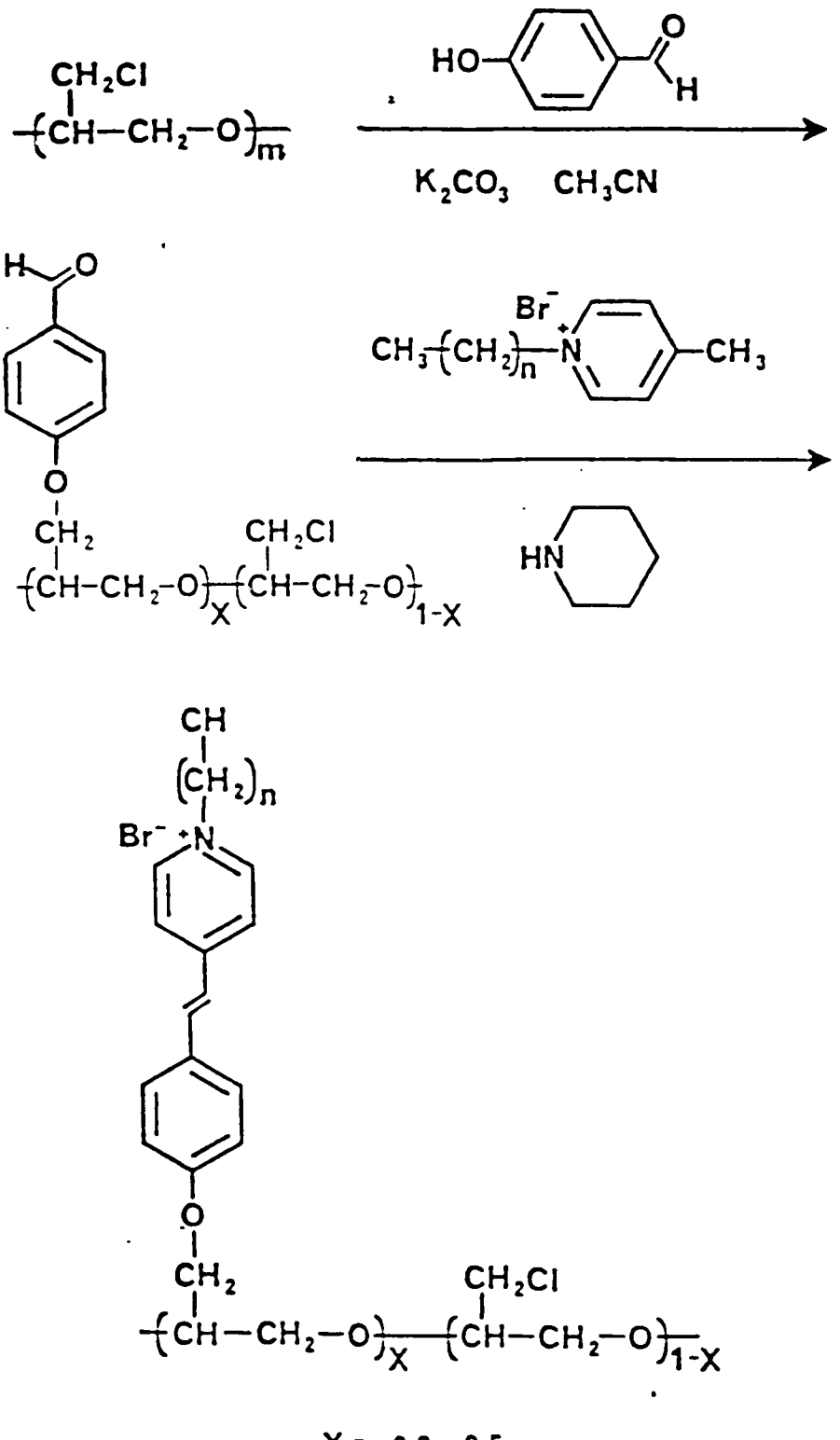
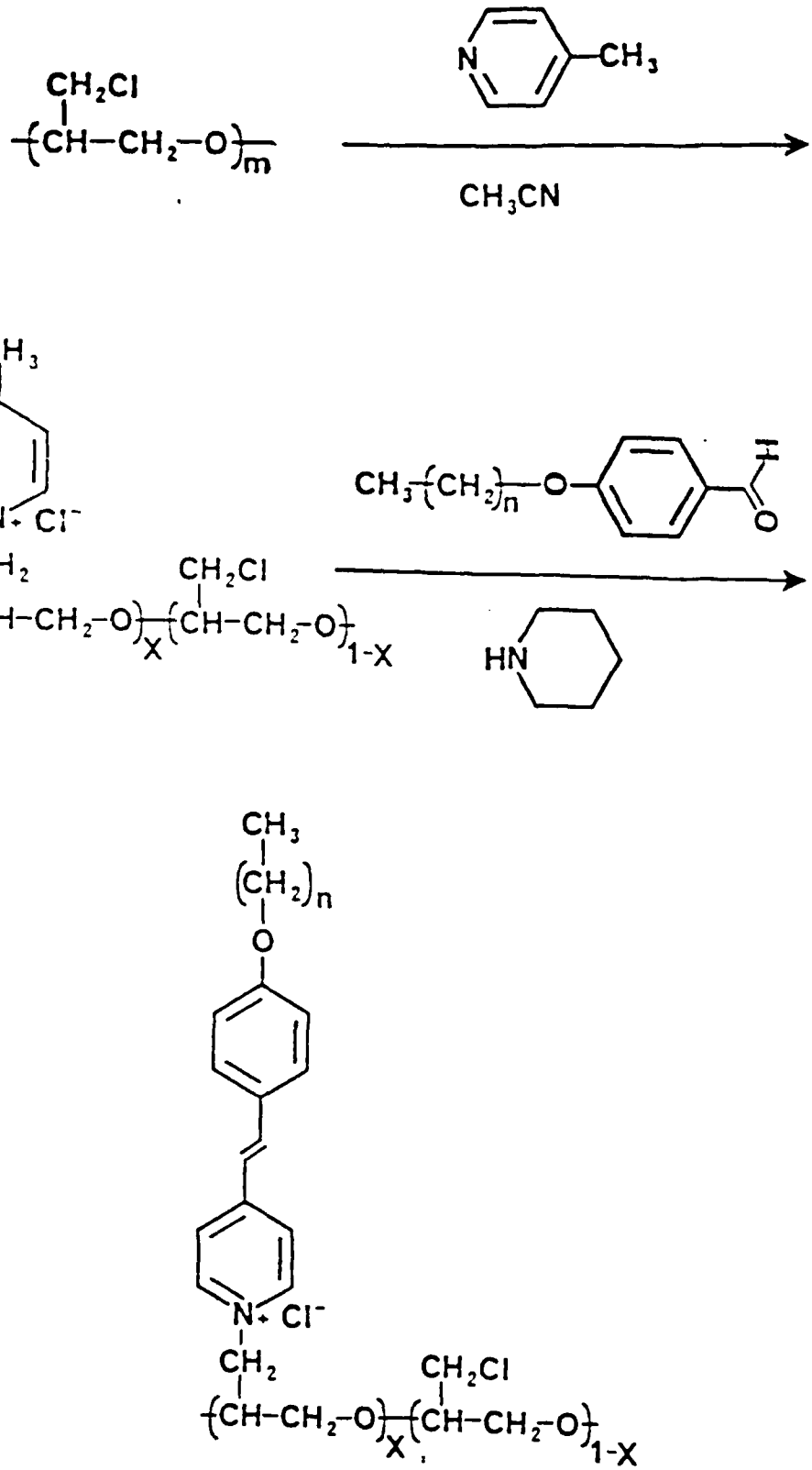



Figure 2. Langmuir-Blodgett film deposition shown as (a) monolayer on the water surface, (b) deposition of first monolayer onto substrate during upstroke, (c) deposition of second layer (downstroke), and (d) three layers after second removal of substrate.




Scheme I. Synthesis of hemicyanine-substituted PECH with electron donating group adjacent to polymer backbone.



Scheme II. Synthesis of hemicyanine-susbtituted PECH with electron withdrawing group adjacent polymer backbone.

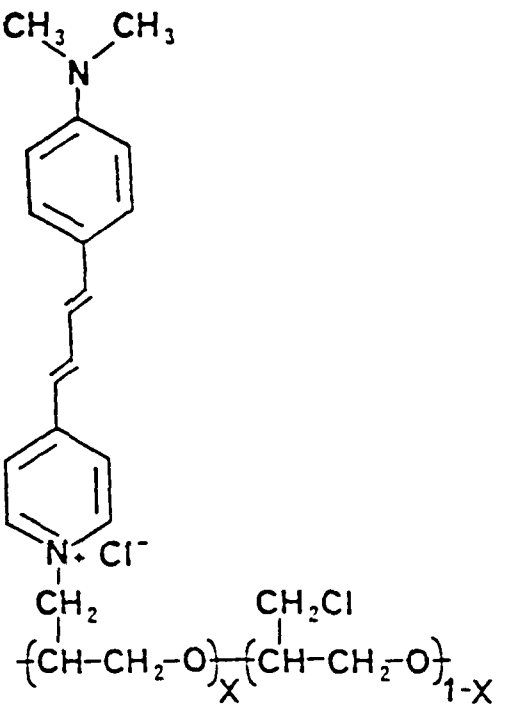


Figure 3. PECH substituted with a hemicyanine chromophore containing an extended pi-electron system.

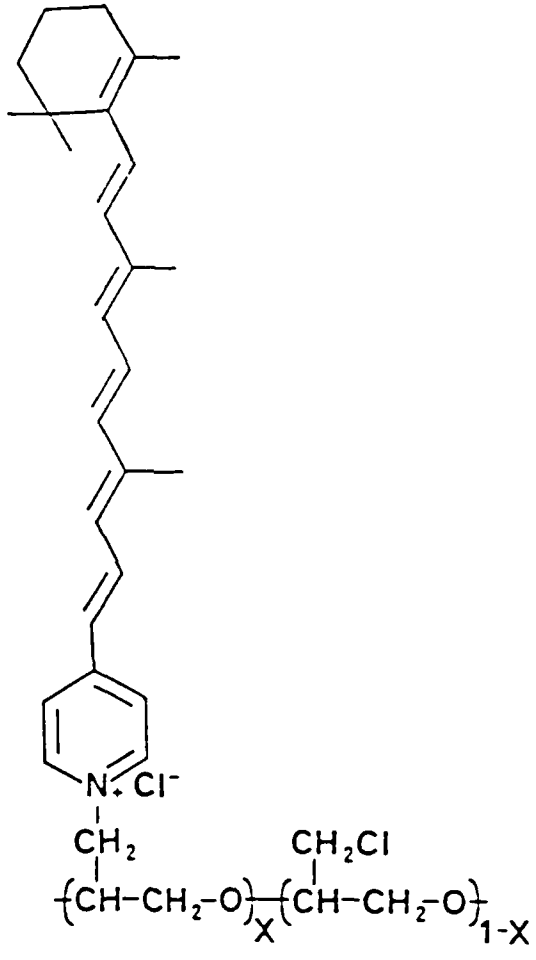
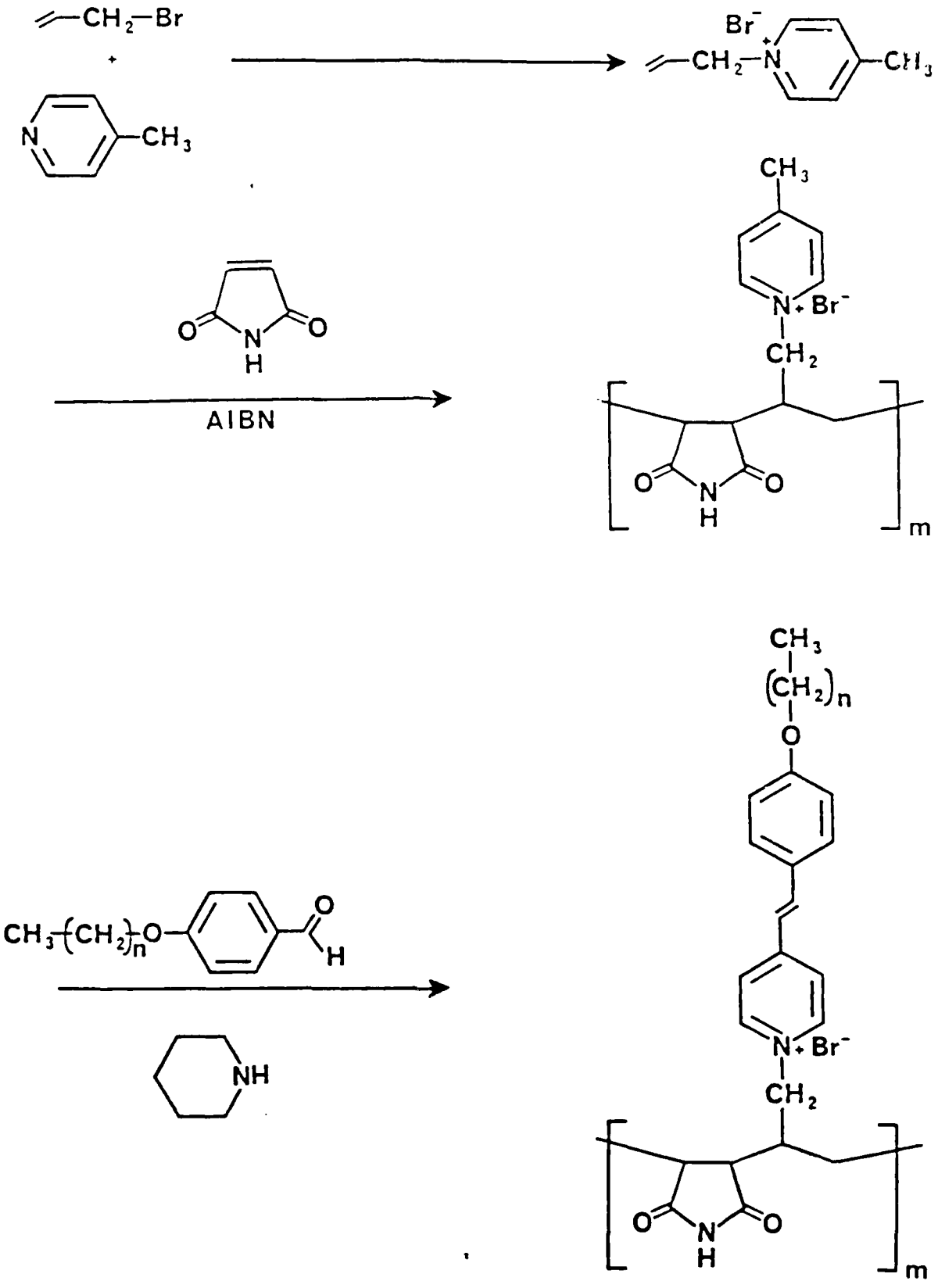


Figure 4. PECH substituted with a rhodopsin-like chromophore.




Scheme III. Synthesis of maleimide-allyl hemicyanine alternating copolymer.

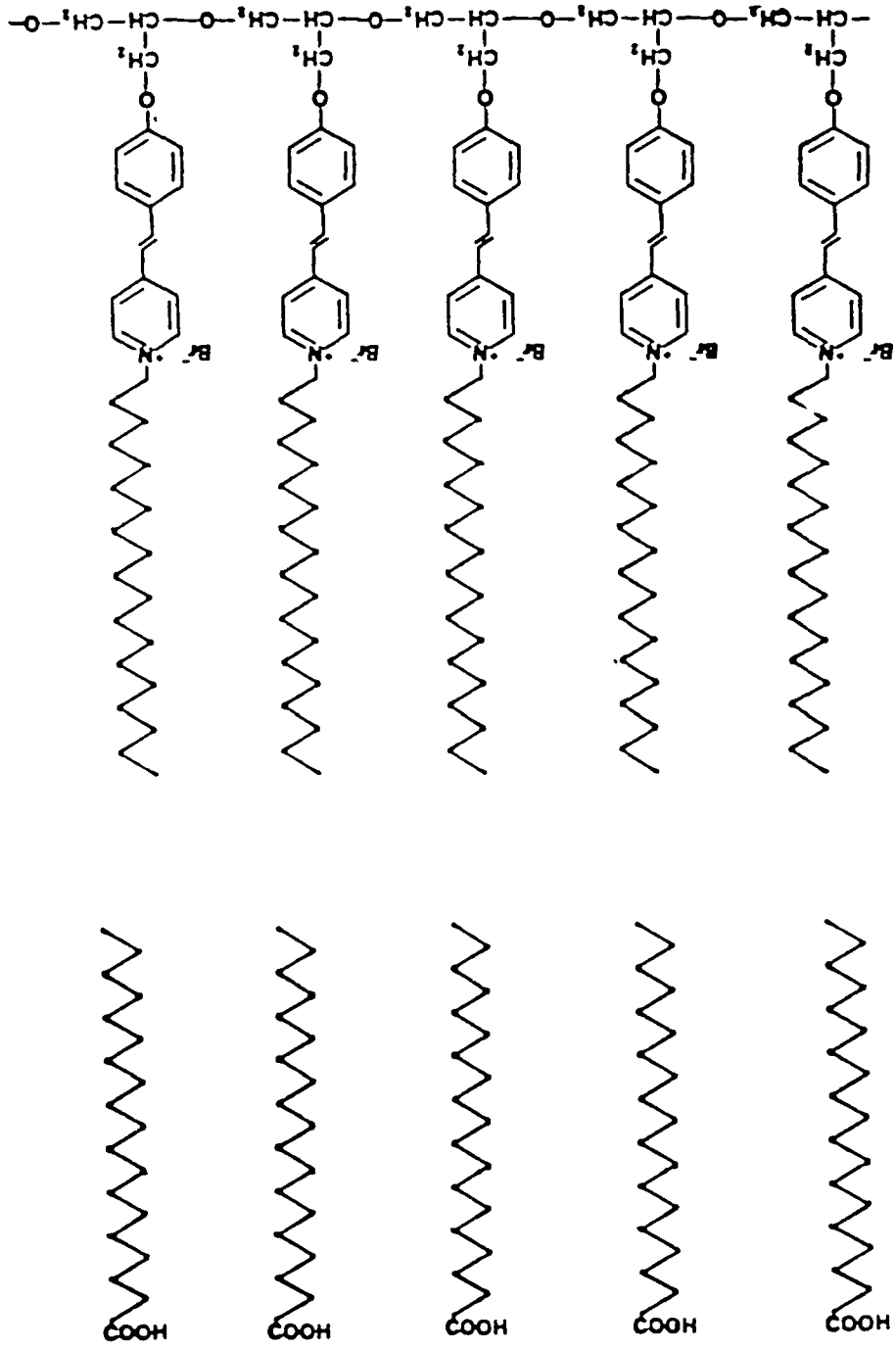



Figure 5. Alternating layer structure of PECH-hemicyanine (polymer A) with behenic acid.

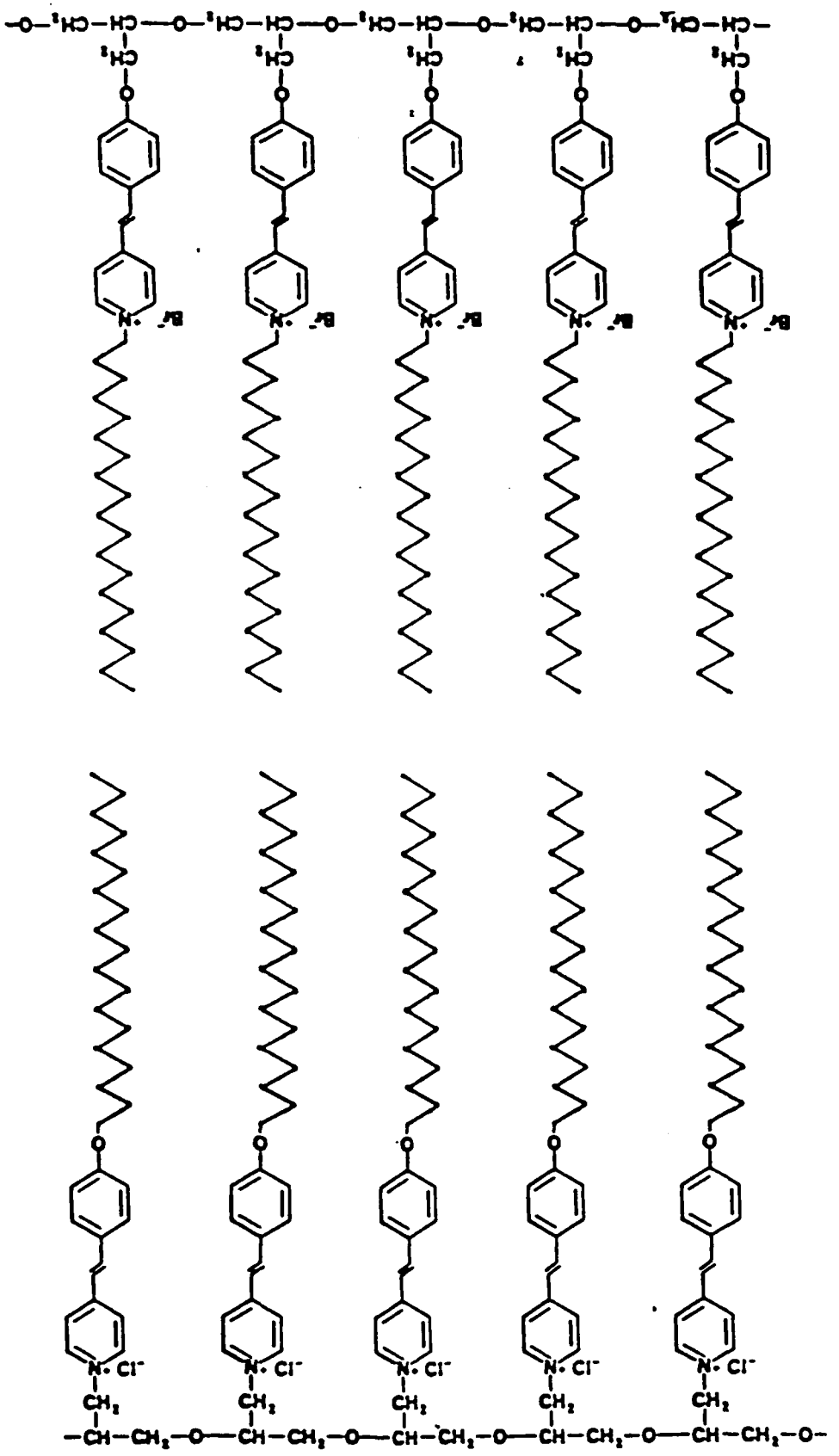


Figure 6. Alternating layers of polymers A and B.

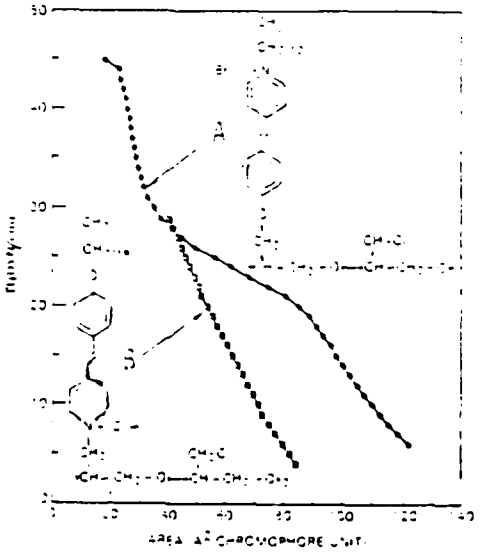


Figure 7. Surface pressure vs. surface area (pi-A) curve for PECH-hemicyanines A and B.

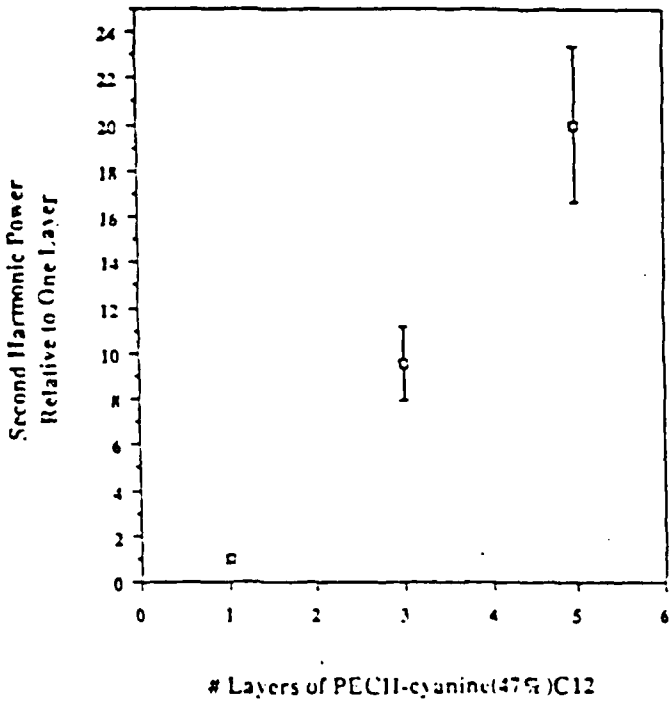



Figure 8. Enhancement of second harmonic signal vs. number of layers for PECH-hemicyanine type A interleaved with behenic acid.

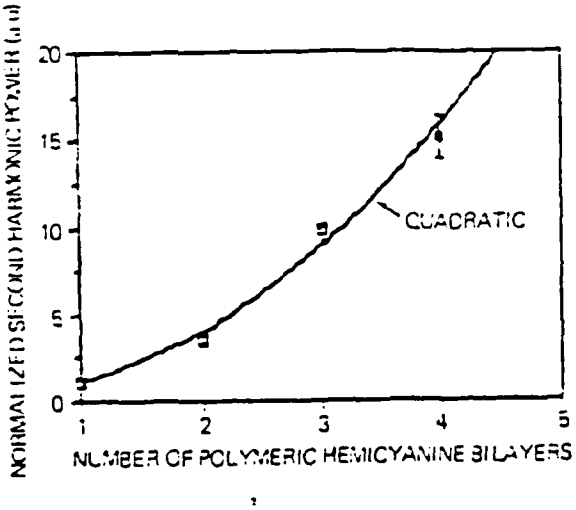



Figure 9. Enhancement of second harmonic signal vs. number of bilayers of interleaved polymer A and B.

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